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# **Evaluation of X-ray Fluorescence Analysis for the Determination of Arsenic, Vanadium, Cadmium, Lead and Mercury in Various Matrices**

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National Bureau of Standards  
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Prepared for  
**Environmental Protection Agency**  
**Research Triangle Park, North Carolina 27711**



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**U.S. DEPARTMENT OF COMMERCE, Juanita M. Kreps, *Secretary***

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ABSTRACT

Limits of detection for arsenic, vanadium, cadmium, lead and mercury have been determined with a wavelength-dispersive or energy-dispersive x-ray spectrometer, or with both, in various matrices consisting of cupric oxide, ferric oxide, lead oxide, coal and fly ash.

1. INTRODUCTION

The limits of detection have been determined for arsenic in cupric oxide and in ferric oxide, for vanadium in cupric oxide, ferric oxide, lead oxide, coal, and in fly ash, for cadmium in cupric oxide, for lead in cupric oxide and in ferric oxide, and for mercury in coal. Limits of detection for mercury in coal have already been determined and reported in NBSIR 75-675 and are included as an addendum to this report. Measurements were made with either a wavelength-dispersive x-ray spectrometer or an energy-dispersive instrument, or, in some cases, with both. Samples were prepared by adding known amounts of NBS Standard Reference Materials to the matrix of interest and grinding to obtain a homogeneous sample. To obtain concentrations of an element in the 10 to 100 ppm range, successive dilutions of the sample with the matrix material followed by grinding were required.

2. EXPERIMENTAL

The energy-dispersive instrumental arrangement used in this work differed to some extent from that described previously [1]. A commercially available system was used consisting of a tungsten target x-ray tube for exciting various secondary emitters. These consisted of titanium,

Table 1. Instrumental Conditions

Sample <sup>a</sup>	Wavelength Dispersive <sup>b</sup>		Energy Dispersive		Live <sup>d</sup> Time in Seconds	In Air	In Vac.
	X-ray Conditions	Bragg Crystal	Counting Time in Seconds	W Tube Conditions			
As in CuO	Mo- 45kV, 45mA	LiF	500	30kV, 10mA	Mo <sup>c</sup>	yes	--
As in Fe <sub>2</sub> O <sub>3</sub>	--	--	--	30kV, 25mA	Mo	yes	--
V in CuO	Mo- 47kV, 47mA	Graphite	500	25kV, 10mA	Ni	--	yes
V in Fe <sub>2</sub> O <sub>3</sub>	Pt- 48kV, 48mA	LiF	500	--	--	yes	--
V in Coal	--	--	--	20kV, 3.5mA	Ni	--	yes
V in Fly Ash	--	--	--	20kV, 3.5mA	Ni	--	yes
Cd in CuO	Cr 40kV, 25mA	Graphite	500	--	--	yes	--
Pb in CuO	Mo 45kV, 45mA	LiF	500	31kV, 11mA	Mo	yes	--
Pb in Fe <sub>2</sub> O <sub>3</sub>	--	--	--	30kV, 17mA	Mo	yes	--

<sup>a</sup>X-ray lines measured were as follows: AsK $\alpha$ , VK $\alpha$ , CdL $\alpha$ , and PbL $\alpha$ .

<sup>b</sup>Collimation: 102 mm (in length) X 0.51 mm (spacing) + 15.8 mm X 0.25 mm.

<sup>c</sup>Mo secondary emitter including a Mo thin foil filter.

<sup>d</sup>Live time is actual counting time corrected for dead time. That is: Live time  $\approx$  1.5 X clock time.

nickel, molybdenum and tin, which were very effective because these monochromatic x-ray lines could be selected to provide the most efficient excitation conditions for analysis of the elements in the sample. A 16-position sample holder was also constructed at NBS in order to obtain good reproducibility on replicate measurements. The instrumental conditions used for each type of spectrometer are summarized in table 1.

Samples were prepared by addition of known amounts of NBS-SRM's or pure reagents to the various matrices of interest followed by grinding in a mortar and pestle. In table 2 is a summary of the reagents employed. Successive dilution of the samples with the matrix was performed to obtain concentrations of an element in the 10-100 ppm range. One-gram samples of the powders were then added to Somar\* cups and subsequently analyzed.

Table 2. Known Samples

<u>NBS-SRM No.</u>	<u>Compound Name</u>
83c	Arsenic trioxide
1052b	13.0% V in Bis(1-phenyl-1, 3-butanediono) oxovanadium (IV)
1053a	24.8% Cd in cadmium cyclohexanebutyrate
1059b	36.7% Pb in lead cyclohexanebutyrate

The organo-metallic compounds were selected because of their relatively low concentrations of the element of interest. These required fewer dilutions to be made in order to obtain concentrations in the low ppm range. The copper oxide matrix was prepared from oxidation of copper metal

\*Certain commercial equipment, instruments or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.

(NBS-SRM 45d). The ferric oxide and lead oxide were analytical reagent grade, and the coal and fly ash were NBS-SRM's 1632 and 1633, respectively.

### 3. MEASUREMENTS AND RESULTS

The limit of detection is often used to characterize the sensitivity of a particular analytical technique for certain trace analysis problems. Because of the numerous and sometimes inconsistent definitions of a detection limit that appear in the literature (see reference 2 for example), it is important to specify how it is defined. For the purpose of this report, the method proposed by Currie [2] is used. An equation can be written for a detection limit based on Poisson counting statistics such as

$$C_{t\ell} = C_{STD} \frac{4.65\sqrt{N_o}}{N_{STD} - N_o} \quad (1)$$

where  $C_{t\ell}$  is the lowest limit of detection theoretically obtainable of the element of interest for a single measurement in concentration units (ppm);  $C_{STD}$  is the known concentration (ppm) of that element in the standard;  $N_o$  is the total number of counts corresponding to the background or blank in some known time interval; and  $N_{STD}$  is the total number of counts (i.e., gross counts) from the standard in the same time interval. Substitution of x-ray intensities for the background and net signal intensities of the standards in the above equation yields a concentration level which should lead to a detected result with 95% confidence. This equation is identical to the one which appears in a previous report [1] except for the numerical constant 4.65. This constant is used when as few as two measurements are made of the background and sample (e.g., paired observations). The quantity  $(N_{STD} - N_o)/C_{STD}$  is usually referred to as the sensitivity in  $\text{ppm}^{-1}$  and is tabulated along with x-ray intensity data in table 3.

Table 3. Data Summary

Samples	Conc. ppm	Wavelength-Dispersive					$t_{.95}^g$	$N_o^{1/2}$	Sensitivity ppm <sup>-1</sup>
		Net peak counts (av)	Background counts (av)	$n^e$	$s$ (counts) <sup>f</sup>				
As(CuO)	10,000	--	--	--	--	--	--		
	250	19,533							
	100	9,398						97	
	50	5,299	33,522	10	200	1.833	183		
	10	1,930							
As(Fe <sub>2</sub> O <sub>3</sub> )	200	--	--	--	--	--	--	--	
	50								
V(CuO)	50	21,893	173,752	3	1200	2.920	417	438	
V(Fe <sub>2</sub> O <sub>3</sub> )	100	13,538	18,740	5	61	2.132	137	143	
	50	7,558							
V (coal)	17.5	--	--	--	--	--	--	--	
	7.0								
V (fly ash)	70								
	35	--	--	--	--	--	--	--	
	14								
V(PbO)	200	--	--	--	--	--	--	--	
Cd(CuO)	250	3,229	22,191	7	127	1.943	149	13	
Pb(CuO)	125	5,319	35,409	3	136	2.920	188	42.5	
Pb(Fe <sub>2</sub> O <sub>3</sub> )	200	--	--	--	--	--	--	--	
	100								
	50								

## Energy-Dispersive

As(CuO)	10,000	23,718						
	250	643						
	100	260	94	3	12.9	2.920	9.7	2.6
	50	140						
	10	41						
As(Fe <sub>2</sub> O <sub>3</sub> )	200	629						
	50	242	236	3	13.7	2.920	15.4	4.0
V(CuO)	50	4,901	5,500	4	56	2.353	74	98.0
V(Fe <sub>2</sub> O <sub>3</sub> )	100							
	50	--	--	--	--	--	--	--
V (coal)	17.5	10,217	4,223	4	84	2.353	65	536
	7.0	2,766						
V (fly ash)	70	38,030						
	35	28,849	11,193	4	280	2.353	106	543
	14	14,554						
V(PbO)	200	2,515	1,472	3	56	2.920	38	12.6
Cd(CuO)	250	--	--	--	--	--	--	--
Pb(CuO)	125	245	105	3	13	2.920	10.2	1.8
Pb(Fe <sub>2</sub> O <sub>3</sub> )	200	861						
	100	364	311	9	18	1.860	16.8	4.0
	50	83						

<sup>e</sup> $n$  is the number of replicate measurements of the background.

<sup>f</sup> estimated standard deviation of a single measurement of the background.

<sup>g</sup> Student's  $t$  based on  $(n-1)$  degrees of freedom.

A limit of detection based on measurement data can also be calculated according to reference [2], if the variability of the blank is known or can be measured. If  $n$  replicate measurements of the blank are made and the standard deviation (i.e.,  $s$ ) of a single measurement is computed, then an experimental limit of detection ( $C_{exp}$ ) can be calculated according to the equation

$$C_{exp} = C_{STD} \frac{2\sqrt{2} t s}{N_{STD} - N_0} \quad (2)*$$

where  $t$  is Student's  $t$  [3] based on  $n-1$  degrees of freedom. Limits of detection for arsenic, vanadium, cadmium, and lead were calculated according to the above equations and are tabulated for comparison in table 4.

It is interesting to compare the variability of the background tabulated in table 3 for each type of spectrometer. Of course, if the variability is computed according to equation 1, where it is equal to  $N_0^{1/2}$ , then the only contribution to the random error is assumed to be due to the Poisson statistics of error. The limit of detection calculated in this manner represents the lowest limit theoretically obtainable. If the standard deviation is computed such as in equation 2, then the total contribution to the random error is included in the calculation of the detection limit and will necessarily include experimental sources of random error (e.g., the effect of ambient temperature variations). It should be emphasized, however, that systematic error is not included in these calculations and should be considered separately.

Comparison of the computed standard deviation (i.e., column 6, table 3) with the  $N_0^{1/2}$  values via the chi-square test indicated that the Poisson error is the primary contribution to the random error in most cases. The chi-square

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\*The factor  $2\sqrt{2}$  is due to comparison of the unknown with the blank, and that  $L_D \approx 2L_C$ .

Table 4. Limits of Detection for As, V, Cd, and Pb in Various Matrices  
 Calculated from Equations 1 and 2

Matrix	As		V		Cd		Pb		
	$C_{t1}$ in ppm	$C_{exp}$ in ppm	$C_{t1}$ in ppm	$C_{exp}$ in ppm*	$C_{t1}$ in ppm	$C_{exp}$ in ppm	$C_{t1}$ in ppm	$C_{exp}$ in ppm	
CuO	(1)	8.8	(1)	4.4	(1)	53	(1)	20.5	26.0
	(2)	17.3	(2)	3.5	(2)	--	(2)	26.4	59.0
Fe <sub>2</sub> O <sub>3</sub>	(1)	--	(1)	4.5	(1)	2.5	(1)	--	--
	(2)	17.9	(2)	--	(2)	--	(2)	19.5	23.0
Coal	(1)	--	(1)	--	(1)	--	(1)	--	--
	(2)	--	(2)	0.56	(2)	1.0	(2)	--	--
Fly Ash	(1)	--	(1)	--	(1)	--*	(1)	--	--
	(2)	--	(2)	0.91	(2)	3.4	(2)	--	--
PbO	(1)	--	(1)	--	(1)	--	(1)	--	--
	(2)	--	(2)	14.0	(2)	36.3	(2)	--	--

(1) wavelength-dispersive

(2) energy-dispersive

\* - variability of background exceeds Poisson contribution

values were exceeded for V in CuO and for V in fly ash, and indicate that the background variability can be attributed to other sources.

Limits of detection for arsenic and lead in coal, and in fly ash could not be accurately determined because of the AsK $\alpha$ -PbL $\alpha$  x-ray line interferences. Efforts to obtain samples of coal and fly ash containing lower concentrations of As and Pb were not successful. Poor results were obtained for cadmium because the background in all cases was very high and the signal level was generally too low with both types of x-ray spectrometers. Vanadium in ferric oxide, however, could not be measured accurately with the energy-dispersive spectrometer because of the interference of the vanadium K $\alpha$  line with the escape peak caused by the FeK $\alpha$  x-ray line.

#### 4. CONCLUSION

The statistical limits of detection for arsenic, vanadium, cadmium and lead were determined in various matrices consisting of copper oxide, iron oxide, lead oxide, coal and fly ash. In general, the lowest limits of detection were obtained for vanadium in the various matrices with an energy-dispersive spectrometer. These results can be explained on the basis of the generally low background in the x-ray energy region of vanadium and the high excitation efficiency of the nickel secondary emitter. In contrast, a high detection limit for cadmium (i.e., 70 ppm) in copper oxide was obtained.

## 5. REFERENCES

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